Besides the ESR studies the viscosity of PET composites was measured before and after \(\gamma\)-irradiation at a dose of 50 kGy. The changes of MFR index are shown in Table. The MFR index increases substantially after irradiation for PET/PP \((90/10)\) proving that in these materials polymer degradation is a major process.

**Conclusions**

The ESR results show that the ability of PET and PP polymers for the stabilization of radicals differs very much. At room temperature the radicals in PET are not stable at all, whereas in PP peroxy radicals are recorded even few days after irradiation with relatively high concentration. It is postulated that the PP ability for peroxy radical formation is associated with the structure and chemical properties of polymer. Interestingly, in PET/PP composites even a small amount of PP (10-20\%) improves the polymer ability for radical stabilization indicating that the radical processes in PET/PP composites have no additive character. This can be understood if PP units are able to stabilize also the radical centers primarily formed in PET units and migrating along the polymer chain.

The changes of MFR index indicate that irradiation of PET and PP polymers as well as of PET/PP composites causes polymer degradation. The degree of polymer degradation seems to correlate with peroxy radicals concentration stabilized at room temperature.

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**References**


**FURTHER STUDIES ON IRRADIATION PRODUCTS AND TOXICITY CHANGES IN RADIOLYTIC DECOMPOSITION OF 2,4-DICHLOROPHENOL**

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Although numerous different technologies are being developed parallel, a radiation technology in environmental cleanup has found already several advantageous practical applications [1, 2]. Economic analysis has been reported for ozone/electron beam process for groundwater remediation, where addition of ozone improves the efficiency by elimination of the reducing species formed simultaneously with the OH free radicals [3]. A practical usefulness of several routinely utilized technologies such as air stripping, biological degradation, or adsorption on activated carbon has various limitations for different organic compounds present, for instance, in effluents from petrochemical industry [4].

Numerous research groups have reported recently studies on radiation decomposition of organic pollutants such as mono-, di-, and trichlorophenols [5], pentachlorophenol [6], chlorinated benzenes [7], trichloroethane and perchloroethylene [8], hydroxybenzoate and hydroxybenzoic ethyl ester [9], EDTA [10] and atrazine [11]. New data have been reported on electron beam treatment of municipal waste water in the aerosol flow [12], on irradiation of industrial effluents [13] and waste water from a molasses processing [14].

This work is a continuation of our earlier research on the radiolytic degradation of chlorophenols [15] and on effect of selected scavengers on the radiolytic degradation of 2,4-dichlorophenol (2,4-DCP) [16], one of the most frequently occurring chlorophenolic pollutant in the environment and product of decomposition of numerous organic biocides.

Irradiation of 100 ml solutions of 2,4-DCP was carried out with a Russian \(\gamma\)-irradiation source fissilewated with \(^{60}\)Co, dose rate 4 kGy h\(^{-1}\) and mean energy 1.25 MeV in glass conical flasks of 150 ml volume. In part of the studies a cobalt source Gammacell (Canada) at a dose rate 6.85 kGy h\(^{-1}\) was employed with irradiation of 50 ml samples in glass vials. Reversed-phase HPLC and ion-chromatography measurements were carried out in experimental conditions described earlier [16]. Bioindicative measurements of toxicity based on bioluminescence of bacteria Vibro fisheries [17] were carried out using a Microtox M500 Toxicity Analyser MICROTOX from Azur Environment (Berkshire, Great Britain). The determination of total organic content (TOC) was performed in the Institute of Energetics and Nuclear Research IPEN in Sao Paulo, Brazil, using Shimadzu TOC-5000 analyzer.

The reversed-phase chromatographic measurements provided new information about the effectiveness and mechanism of radiolytic degradation of 2,4-DCP in various experimental conditions. At doses not exceeding 1 kGy the yield of decomposition essentially depends on the initial concentration of 2,4-DCP. For 50 ppm 2,4-DCP only 40\% has been decomposed, and a dose of 10 kGy is needed for complete decomposition. The efficiency of radiolytic degradation is additionally decreased in the
The presence of scavengers such as nitrate. The presence of 20 ppm nitrate at a 1 kGy dose results in a decrease of degradation yield of 20 ppm 2,4-DCP by as much as 60%, and a complete degradation in such conditions requires a 20 kGy dose.

The results of total organic carbon (TOC) measurements indicate, however, that even such a large dose does not lead to complete mineralization of the irradiated 20 ppm solutions of 2,4-DCP (Fig.1). For aqueous solutions of 2,4-DCP without any addition only about a 20% decrease of TOC was found. The presence of 50 ppm humic acid practically does not affect the degree of mineralization, while the presence of 20 ppm nitrate decrease this efficiency of complete mineralization to 10%.

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The high-performance ion-chromatography measurements provide more information about the mechanism of 2,4-DCP degradation and other side processes. An example chromatogram shown in Fig.2 was recorded for 20 ppm solution of 2,4-DCP in the presence of bicarbonate irradiated to a dose of 10 kGy. The determination of chloride indicates that at doses of 1 kGy only 50% of chlorine is released from organic compounds as inorganic chloride ion. At 10 kGy, however, only 10 to 15% chlorine, depending on the initial concentration of 2,4-DCP, is converted into chloride. In the presence of 50 ppm nitrate about 70% of dehalogenation of organic species was observed for 20 ppm 2,4-DCP solution at 10 kGy, while complete degradation has been observed at 20 kGy (Fig.3). The presence of 10 to 50 ppm of humic acid practically does not influence the release of inorganic chloride.

It was already shown that even a 20 kGy dose does not cause total mineralization of 2,4-DCP at a 20 ppm level. According to earlier suggestions of Getoff and Solar [18] dehalogenation of 4-chlorophenol leads to the formation of di- and tribromoxybenzenes, and then to the opening of aromatic ring and formation of various carboxylic acids. A similar mechanism can be expected in case of

2,4-DCP and the presence of several carboxylic acids was found in this study in ion-chromatography measurements of irradiated 2,4-DCP solutions. At doses above 0.5 kGy the presence of formic and acetic acids was observed in irradiated samples. In the presence of 50 ppm bicarbonate a 4-fold increase of the concentration of propionate and the presence of acetate were found at a dose increase from 1 kGy to 10 kGy (Fig.2).

Several additional processes have been observed during irradiation of 2,4-DCP solutions containing nitrate. At its content 10 to 20 ppm and a 1 kGy dose, about 50% of the nitrate undergoes radiolysis and 0.5 to 1.6 ppm nitrite is formed. At higher doses the nitrite is decomposed, however, in the nitrate presence of 50 ppm its radiolysis leads to the formation of about 10 ppm of nitrite even at a 20 kGy dose (Fig.3). At this initial level of nitrate cation-chromatography allows to detect 13 to 16 ppm ammonium in 2,4-DCP solutions irradiated to 1-5 kGy doses.

Fig.1. Relative changes of total organic carbon content in irradiated 20 ppm solution of 2,4-DCP at pH 7.0.

Fig.2. Ion-chromatogram obtained for solution containing 20 ppm 2,4-DCP in the presence of 50 ppm bicarbonate at pH 7.0 after irradiation to dose 10 kGy. See text for chromatographic conditions.

Fig.3. Ion-chromatographic determination of chloride, nitrate and nitrite in 20 ppm solution of 2,4-DCP at pH 7.0 containing 50 ppm nitrate during irradiation to different doses.
The fundamental purpose of radiation treatment of polluted waters or wastes is not only decomposition of particular species, but first of all a decrease of total toxicity of these solutions. In this stage of the study additional investigations were initiated to examine toxicity using widely used bioluminescence test Microtox®, which was already employed for the determination of toxicity of numerous chemical compounds [19]. As a function of applied dose up to 20 kGy, the changes of toxicity of 2,4-DCP solutions were examined without and with addition of other substances or laboratory wastes from this Institute spiked with 20 ppm 2,4-DCP (Fig. 4). At a 20 ppm 2,4-DCP level a complete reduction of toxicity has been obtained at 10 kGy dose, while for 50 ppm 2,4-DCP solution a certain residual level of toxicity was found even at a 20 kGy dose (Fig. 4B). The presence of nitrate decreases the reduction of toxicity with increasing dose (Fig. 4C). Both in the absence of nitrate, and especially in its presence at a low radiation dose up to 1 kGy a certain initial increase of toxicity has been found (at 50 ppm nitrate even about 60%). This can be explained by the formation at low doses of polyhydroxybenzenes, much more toxic against bacteria used in Microtox than 2,4-DCP. For instance, the toxicity of hydroquinone is about two orders of magnitude higher than 2,4-DCP [19]. Also inorganic nitrogen compounds with reducing properties formed in the radiolysis of nitrate are also highly toxic. A substantial increase of toxicity at a 1 kGy dose is favoured by the presence of excess of chloride as well as humic acid (Fig. 4A). Changes of toxicity of non-radioactive laboratory waste containing 500 ppm chloride and 5.0 ppm nitrate and spiked with 20 ppm 2,4-DCP were also examined. The irradiation to dose 20 kGy has reduced its toxicity only by 50% (Fig. 4A).

The broadening of chromatographic diagnostics of radiolytic degradation of 2,4-DCP with TOC and toxicity measurements allows to make additional conclusions on this method of water and waste treatment. Because of side effects of various scavengers and a different toxicity of various compounds formed during radiolysis, doses estimated for effective radiolytic degradation of given pure chemical species usually require a significant increase in practical applications. Further studies should be focused on the determination of doses for complete mineralization of wastes, or at least for sufficient reduction of their toxicity.

References